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Growth of β-Ga_2O_3 nanorods by ammoniating Ga_2O_3/V thin films on Si substrate*

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This paper reports that β-Ga_2O_3 nanorods have been synthesized by ammoniating Ga_2O_3 films on a V middle layer deposited on Si(111) substrates. The synthesized nanorods were confirmed as monoclinic Ga_2O_3 by x-ray diffraction, Fourier transform infrared spectra. Scanning electron microscopy and transmission electron microscopy reveal that the grown β-Ga_2O_3 nanorods have a smooth and clean surface with diameters ranging from 100 nm to 200 nm and lengths typically up to 2 μm. High resolution TEM and selected-area electron diffraction shows that the nanorods are pure monoclinic Ga_2O_3 single crystal. The photoluminescence spectrum indicates that the Ga_2O_3 nanorods have a good emission property. The growth mechanism is discussed briefly.

Keywords: β-Ga_2O_3 nanorods, vapour–solid mechanism, V
PACC: 6146

1. Introduction

Since the discovery of carbon nanotubes,[1] one-dimensional nanometre-sized materials have attracted much attention due to their great potential for fundamental studies as well as for application in low cost, small-sized, and low power consumption devices. To date, various kinds of materials such as Si, Ge, silica, MgO, CaO, GaN, β-SiC and ZnO were synthesized as nanowires and a number of methods were tried for fabricating the nanowires.[2−7] Monoclinic gallium oxide (β-Ga_2O_3) is one of the important wide band gap ($E_g \approx 4.9$ eV) semiconductors which show good chemical and thermal stability and interesting luminescence properties.[8] β-Ga_2O_3 nanostructures such as nanorods are currently the subject of intense research because of their potentials for nanoscale electronic and optoelectronic devices.[9,10] Different workers synthesized nanoscaled β-Ga_2O_3 in powder form by different methods such as physical evaporation of Ga_2O_3 via a vapour–solid (VS) process,[7] milling of GaN powders,[11] annealing of GaAs in dry oxygen atmosphere,[12] a vapour–solid method exploiting a catalytic growth process,[13] silica-assisted Fe catalytic growth,[14] thermal reaction between pure Ga_2O_3 and active carbon,[15,16] and alumina-assisted catalytic growth.[17]

In this work, we report a successful synthesis of highly crystalline Ga_2O_3 nanorods through ammoniating Ga_2O_3/V films on Si(111) substrate deposited by radio frequency (RF) magnetron sputtering system.

2. Experimental details

The β-Ga_2O_3 nanorods were prepared by a two-step method. The first step was to deposit Ga_2O_3/V films on Si(111) substrate in turn using a JCK-500A magnetron sputtering system (13.56 MHz). The targets for depositing V films and Ga_2O_3 films were hot-pressed V with a purity of 99.9% and sintered $Ga_2O_3$with a purity of 99.99%.The base pressure before sputtering was about 1.2×10^{-3} Pa. The working gas was pure argon and the working pressure was 3 Pa. The distance between the target and the substrate was 8 cm. When V was deposited, the output voltage of Wen Liu Yuan (WLY) steady current device was 315 V and the output current was 160 mA. It was different that Ga_2O_3 films were deposited through RF magnetron sputtering. The sputtering power was 150 W. The sputtering progress was maintained at room temperature by using the cooling system. The thickness was about 60 nm for V films and 500 nm for Ga_2O_3 films.

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Subsequently, the Ga_2O_3/V films were ammoniated with a flow rate of 500 ml/min in a horizontal tube furnace. The temperature and the duration of the ammoniating were 950°C and 10 min, respectively.

The samples were measured with x-ray diffraction (XRD, Rigaku D/max-rB Cu Kα) meter to specify their crystalline structures. Fourier transformed infrared spectra (FTIR, Tensor27) meter was used to measure the samples' chemical states. Scanning electron microscopy (SEM, Hitachi S-570) and high-resolution transmission electron microscope (HRTEM, Philips TECNAI-20) were carried out at room temperature to measure the products' morphology and microstructure, respectively.

3. Results and discussion

3.1. XRD analysis

Figure 1 depicted the XRD spectrum of a β-Ga_2O_3 nanorod deposited on the silicon substrate. The sharp diffraction peaks in the pattern indicated a monoclinic structure, in agreement with the reported data of bulk β-Ga_2O_3 with lattice constants $a = 1.223$ nm, $b = 0.304$ nm, $c = 0.580$ nm and $\beta = 103.7°$. There is only one peak of the VO_2 at $2\theta = 33.9°$ ($d = 0.264$ nm). No diffraction peaks from GaN, V or other crystalline impurities were found in any of our samples, indicating that the sample was of high purity. And the sharp diffraction peaks also revealed that the β-Ga_2O_3 nanorods thus prepared had a high crystalline quality.

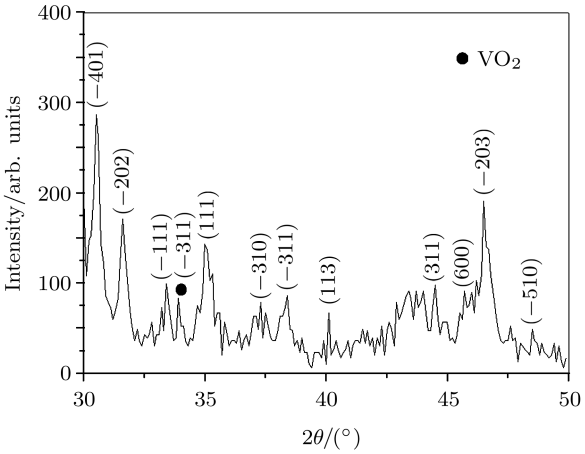


Fig.1. XRD pattern of the synthesized β-Ga_2O_3 nanorods.

3.2. SEM analysis

Figure 2 shows the typical SEM images of the synthesized samples at different magnifications. At the low magnification, it can be clearly observed from Fig.2(a) that a great deal of rod-like structure are interlaced each other and randomly distributed on the surface of the silicon substrate. The whole film surface is actually covered with a layer of β-Ga_2O_3 nanorods by the all-around observation of the SEM. The SEM image of Fig.2(b) demonstrates that the nanorods possess a very smooth surface and a diameter of about from 100 nm to 200 nm and a length of about 2 μm.

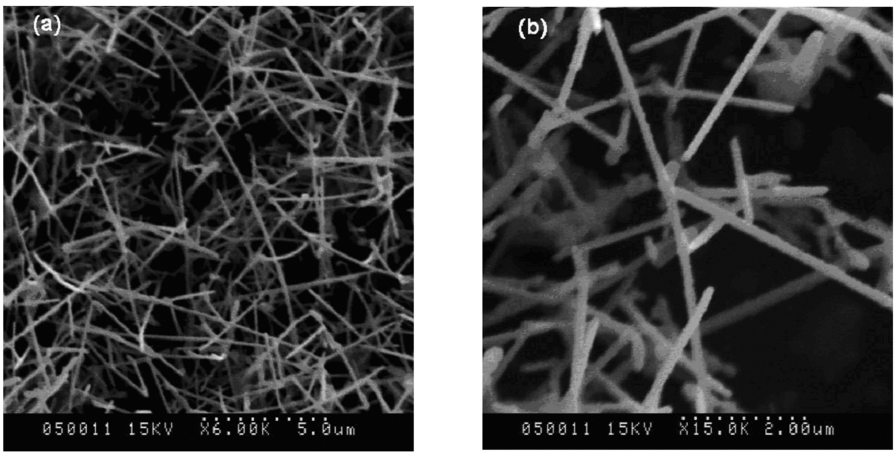


Fig.2. SEM image of the β-Ga_2O_3 nanorods at different magnifications.

3.3. FTIR analysis

The FTIR transmission spectrum of the product is shown in Fig.3. Three prominent infrared absorption bands were observed at 458.92, 609.08 and 1094.50 cm^{-1}, respectively. In the light of the reported band of Ga-O stretching vibration absorption in monoclinic Ga_2O_3 at 465 cm^{-1},[18] the band at 458.92 cm^{-1} should be a Ga–O stretching vibration absorption peak. This also illustrates that the Ga_2O_3 has a monoclinic structure. The sharp absorption band at 609.08 cm^{-1} is due to the local vibration of the substitutional carbon in the Si substrate crystal lattice.[19] The absorption band at 1094.50 cm^{-1} should be attributed to the Si-O-Si asymmetric stretching vibration in the SiO_2 resulted from oxygenation of Si substrate surface.[20]

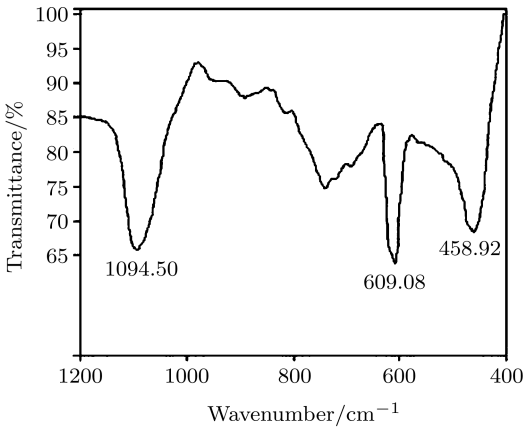


Fig.3. FTIR transmission spectrum of the synthesized β-Ga_2O_3 nanorods.

3.4. Photoluminescence(PL) analysis

PL spectrum of β-Ga_2O_3 product presented in Fig.4 is detected with He–Cd laser used as the excitation source (with a wavelength of 325 nm) at room temperature. Only a broad peak centred at 468 nm (belongs to blue light range) can be activated. Harwig and Kellendouk once proposed that the blue emission was due to the recombination of an electron on a donor formed by oxygen vacancies.[21] Vasil'stiv *et al* suggested that the acceptor should be formed by a gallium–oxygen vacancy pair.[22] For the present β-Ga_2O_3 nanostructures, a huge number of oxygen vacancies and gallium–oxygen vacancy pairs may be formed readily. It should be put forward that in some investigations on PL of gallium oxide crystal or nanorods, not only blue but also ultraviolet emission has been found.[23,24] A similar peak at 475 nm was reported by Liang *et al*[25] in their β-Ga_2O_3nanowires sample. The PL feature of the β-Ga_2O_3 nanorods reported here is quite consistent with the model[26] and peak position reported earlier.

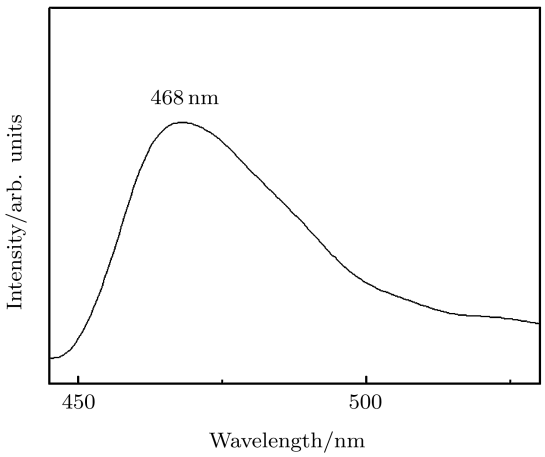


Fig.4. PL spectrum of β-Ga_2O_3 nanorods at room temperature. The wavelength of He–Cd laser is 325 nm.

3.5. HRTEM analysis

Figure 5(a) shows the TEM image of a single β-Ga_2O_3 nanorod with a diameter of 180 nm, providing more structural information. It is straight and has a fairly clean surface. Figure 5(b) shows a HRTEM lattice image of another β-Ga_2O_3 nanorod. The well-spaced lattice fringes in the image indicated a single crystal structure of the nanorod. The white arrow indicated the growth direction of the nanorod. The space between two fringes is about 0.282 nm which corresponds to the distance between the $(\bar{2}02)$ planes, indicating that the growth direction of the nanorod is perpendicular to the fringes of $(\bar{2}02)$ planes. The single-crystal β-Ga_2O_3 nanorod can also be identified from the selected-area electron diffraction (SAED) pattern shown in the inset of Fig.5(b), which can be ascribed to the reflection of monoclinic Ga_2O_3 single crystal.

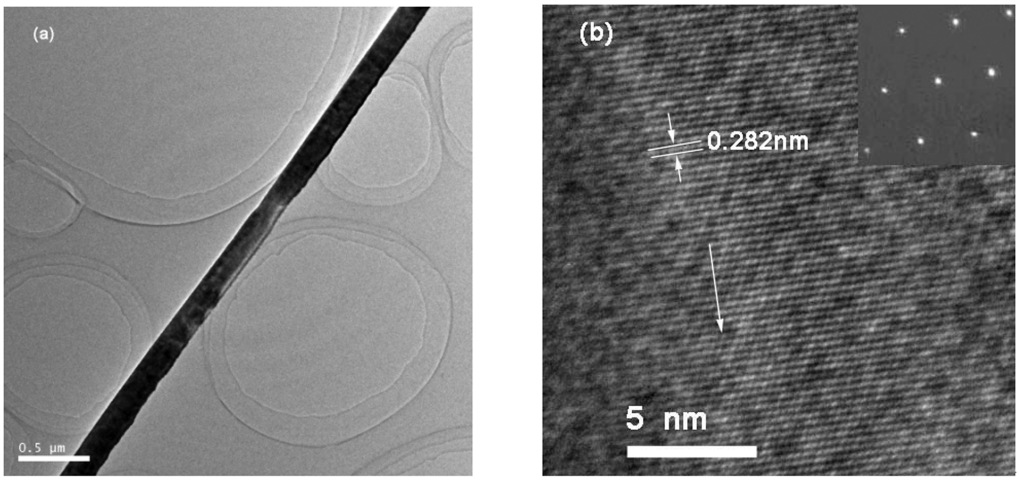


Fig.5. (a) HRTEM image of a single β-Ga_2O_3 nanorod; (b) HRTEM lattice image of the β-Ga_2O_3 nanorod. Inset: the corresponding SAED pattern.

3.6. Discussion about growth process

There are several growth mechanisms developed to explain one-dimensional growth. One is the vapour–liquid–solid (VLS) process,[27] in which nanoparticles as catalyst were capped at the tip of nanostructures. The other is VS mechanism,[28] in which nanostructures were fabricated from the vapour of precursor directly without a liquid state. For the Ga_2O_3 nanostructures synthesized in our cases, VS mechanism is dominant, because no catalysts were involved and observed. We might briefly explain the process as follows. It is well known that Ga_2O_3 begins to decompose into Ga_2O and O_2 above 850°C. V_2O_5, NO_2 and H_2O are subsequently formed through the reaction of metal V with O_2 and NH_3 with O_2. However, V_2O_5 begins to release O_2 over the temperature of 700°C,[29] Ga_2O_3 molecules formed by the reactions of the O_2 with Ga_2O. All the reactions can be expressed as:

$$Ga_2O_3 \rightarrow Ga_2O + O_2,$$
$$V + O_2 \rightarrow V_2O_5,$$
$$NH_3 + O_2 \rightarrow NO_2 + H_2O,$$
$$V_2O_5(l) \rightarrow VO_2(s) + O_2(g),$$
$$Ga_2O(g) + O_2(g) \rightarrow Ga_2O_3(s).$$

There Ga_2O_3 molecules continuously come out and agglomerate into micrograins. When the growth direction of the micrograins are all orientated to the same direction, the single-crystal β-Ga_2O_3 nanorods are formed. However, as the intermedium between Si substrate and Ga_2O_3film, V films are very important for the fabrication of β-Ga_2O_3 nanostructure.

4. Conclusion

In summary, single-crystal β-Ga_2O_3 nanorods were successfully prepared by annealing Ga_2O_3/V films based on VS mechanism. V films are very important for the fabrication ofβ-Ga_2O_3 nanorods. The structure, morphology and optical properties of the as-prepared Ga_2O_3 nanorods are studied by XRD, SEM, HRTEM, FTIR and PL. The PL spectrum at room temperature exhibited a broad peak centred at 468 nm, which may be useful for device application.

References

[1] Lijima S 1991 *Nature* (London) **354** 56
[2] Li Z, Yu T, Yang Z, Feng Y, Zhang G, Guo B and Niu H 2005 *Chin. Phys.* **14** 830
[3] Chang Y, Zhang Y and Zhang Y 2006 *Chin. Phys.* **15** 636
[4] Xue S B, Zhuang H Z, Xue C S, Hu L J, Li B L and Zhang S Y 2007 *Chin. Phys.* **16** 1405
[5] Pan Z W, Dai Z R and Wang Z L 2001 *Science* **291** 1947
[6] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater.* **13** 113
[7] Choi Y C, Kim W S, Park Y S, Lee S M, Bae D J, Lee Y H, Park G S, Choi W B, Lee N S and Kim J M 2000 *Adv. mater.* **12** 746
[8] Binet L and Gourier D 1998 *J. Phys. Chem. Solids* **59** 1241

[9] Chang K W and Wu J J 2003 *Appl. Phys.* A **76** 629
[10] Zhang J and Jiang F H 2002 *Chem. Phys.* **289** 243
[11] Kim B C, Sun K T, Park K S, Im K J, Noh T, Sung M Y, Kim S, Nahm S, Choi Y N and Park S S 2002 *Appl. Phys. Lett.* **80** 479
[12] Liang C H, Meng G W, Wang G Z, Zhang L D and Zhang S Y 2001 *Appl. Phys. Lett.* **78** 3202
[13] Zhang H Z, Kong Y C, Wang Y Z, Du X, Bai Z G,Wang J J, YU D P, Ding Y, Hang Q L and Feng S Q 1999 *Solid state Commun.* **109** 677
[14] Tang C C, Fan S S and Chapelle P Li 2001 *Chem. Phys. Lett.* **333** 12
[15] Gao Y H, Bando Y, Sato T, Zhang Y F and Gao X Q 2002 *Appl. Phys. Lett.* **81** 2267
[16] Gundiah G, Govindaraj A and Rao C N R 2002 *Chem. Phys. Lett.* **351** 189
[17] Zhang J and Jiang F 2003 *Chem. Phys. Lett.* **289** 243
[18] Cho S Y, Lee J W, Park I Y and Kim S 2002 *Mater. Sci. Eng.* B
Cho S Y, Lee J W, Park I Y and Kim S 2002 *Solid-State Mater. Adv. Technol.* **95** 275
[19] Sun Y and Miyasato T 1998 *J. Appl. Phys.* **84** 6451
[20] Ding R Q and Wang H 2003 *Mater. Chem. Phys.* **77** 841
[21] Harwig T and Kellendonk F 1978 *J. Solid State Chem.* **24** 255
[22] Vasil'stiv V I and Zakharko Y M 1998 *Prim Ya I. Ukr Fiz Zh* **33** 1320
[23] Lijima S 1991 *Nature* (London) **354** 56
[24] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater* **13** 113
[25] Liang C H, Meng G W, Wang G Z, Zhang L D and Zhang S Y 2001 *Appl. Phys. Lett.* **78** 3202
[26] Binet L and Gourier D 1998 *J. Phys. Chem. Solids* **59** 1241
[27] Sun Y L, Zhang X B and Ning Y S 2002 *J. Inorg. Mater.* **17** 337
[28] Wang M X, Yang L and Wang C M 2004 *Rare Metal Materials and Engineering* **33** 670
[29] Tianjing Academe of Chemical Engineering 2001 *Enchiridion of Abio-fine Chemistry Matter* (Beijing: Publishing Company of Chemical Industry) p891